ELECTRON ENERGY BANDS OF
ONE-DIMENSIONAL RANDOM ALLOYS

DISSERTATION

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To Mary Alice

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Chapter I

INTRODUCTION TO THE PROBLEM

The band structure for a pure solid with crystallographic symmetry has been thoroughly discussed in the literature. All treatments of this topic are based on Bloch's theorem, which states that the one-electron wave function (i.e., the solution of the one-electron Schroedinger equation) for a periodic potential may be written in the form

$$(I, 1) \quad \psi_{\underline{k}}(\underline{r}) = u_{\underline{k}}(\underline{r}) \exp i\underline{k} \cdot \underline{r} \quad ,$$

where $u_{\underline{k}}$ has the periodicity of the one-electron potential. This may be considered as a generalization of Floquet's theorem (see, for instance, page 557 of reference 1),* and rests on firm mathematical ground. Many interesting results in the theory of solids can be obtained in a simple and straightforward way if the dependence of the reduced wave number $\underline{k}$ on the energy of the electron is known.² A number of methods for calculating $\underline{k}(E)$ are available, all resting on the validity of (I, 1). An interesting and

*All bibliographical references appear at the end of this dissertation.

useful result of these calculations is the investigation of "banding." This is the result that the energy intervals in which k is a smooth function of E are separated by intervals in which no normalizable wave functions (and hence no eigenstates of the energy) exist.

Extending these results to the case of an ordered alloy is straightforward in principle. Since the potential is periodic, Bloch's theorem remains valid and the calculations are similar to those for a pure metal. For a disordered alloy (in which two or more different atoms are arranged over the lattice sites in a more or less random way) the situation is altered considerably. Since there is no general mathematical theorem that assures the existence of wave functions of the form $(I, 1)$, the powerful methods that are used on the pure solid are no longer applicable.

Until recently, the attempts to investigate the band structure of random alloys has relied on perturbation theory. The method most widely discussed is the "virtual crystal" model of Nordheim.³ In this model, the true one-electron potential of the disordered alloy is replaced by its average taken over all possible random configurations. This model was justified to the accuracy of first-order perturbation theory by Muto.⁴ In a more recent paper, Parmenter⁵ has estimated the effects of higher-order

perturbation theory, and mentioned some of the limitations on the model. This approach is only expected to hold in the high energy region where the wave function is non-localized, and even there the "virtual crystal" model gives results that are not in agreement with observation.

A new approach to this problem has been given by Korringa.⁶ The method rests on the fact that if the atoms in the crystal are enclosed in polyhedra, separated by regions of constant potential, then the incoming wave to a given polyhedron is the superposition of the outgoing waves from all the other polyhedra. Using equation (I, 1) and evaluating certain lattice sums yields a relation between the incoming and outgoing waves of any polyhedron. Another relation between them is given by solving a scattering problem. For the pure crystal the requirement of consistency on these two relations yields $k(E)$.⁷ For the random alloy, (I, 1) is required to hold in a statistical sense, and the result of the generalization to this case is to give both a relation for $k(E)$ and an effective damping of the incoming waves. In this method the difficulties of perturbation theory are avoided, and the results are of a statistical nature. (This method is applied to a one-dimensional crystal in Chapter III.)

In addition to this work on three-dimensional crystals, there is also an extensive literature on

one-dimensional crystals. (By this is meant the problem of solving a one-dimensional Schroedinger equation for an array of equally spaced potentials.) For the pure crystal (i.e., one potential periodically repeated), the one-dimensional analogue of Bloch's theorem holds. The relation $k(E)$ has been found for many different choices of the potential. The phenomenon of banding is seen in these calculations in its simplest form. The extension to an ordered alloy is again quite straightforward.

The simplest model of a pure one-dimensional crystal is the Kronig-Penney model, which consists of an array of δ -functions multiplied by some constant. An ordered or disordered alloy can be obtained by varying the constant multipliers. This model has been investigated by Saxon and Hutner.⁸

As in the three-dimensional case, the transition to a disordered alloy is complicated by the fact that solutions of the form $(I, 1)$ do not exist. Most of the work on this problem follows along the lines of a paper by James and Ginzburg⁹ in which a method of calculating the number of allowed electron states below a certain energy is given. They first show that the number of allowed bands below a fixed energy is equal to the average number of nodes per unit cell of a real solution of the Schroedinger equation for that energy. A node counting process is then given

which makes it practical to carry out the calculation for a finite crystal on a high speed computer. This leads to a density of states which, for a pure crystal, is usually calculated from $k(E)$. The calculation has been carried out for a random chain of 150 square well potentials with two different well depths by Landauer and Helland.¹⁰ A method for deriving the density of states analytically has been worked out by Schmidt,¹¹ although the computations appear to be feasible only for the case in which the concentration of one of the constituents of the alloy is very low.

The only general theorem about the band structure of random alloys pertains to the special case of δ -function potentials. Saxon and Hutner suggested--and Luttinger¹² proved--that in an energy region in which there are no allowed states for a pure crystal made up of either constituent of a random alloy, there will be none for the alloy.

The purpose of this dissertation is to obtain information about the band structure of random one-dimensional alloys without relying on perturbation theory and without restricting the considerations to a particular arrangement of the atoms. The case of dilute solutions will not be treated, as this problem may be handled by other means (cf. reference 8). As has already been pointed out, the stumbling block to calculations of this kind is that Bloch's

theorem is no longer valid. From a physical point of view, however, it is known that results derived from the consideration of propagating solutions of the form (I, 1) are still valid to a considerable degree for random alloys. Thus the philosophy of the following calculations is to look for solutions that correspond to an over-all transport of electrons through the crystal in a way analogous to the Bloch waves of (I, 1). Another way of stating this is to consider the crystal to be subdivided into a number of equal cells, each containing one atom in the center. Looking at the solutions in each cell, there should be a systematic variation from cell to cell describable by a Bloch wave with reduced wave number k , and random fluctuations superimposed on this.

For the sake of reference, certain general results from the theory of one-dimensional crystals are given in this chapter. Most of these results are discussed in the paper by Saxon and Hutner.⁸

The Schroedinger equation for a one-dimensional crystal may be written in the form

$$(I, 2) \quad \left[\frac{d}{dx^2} + \alpha^2 \right] \psi = \frac{2m V(X)}{\hbar^2} \psi ,$$

where

$$(I, 3) \quad V(X) = \sum_n U_n(X - nd) .$$

In these equations, $\alpha = \sqrt{2mE}/\hbar$ and d is the lattice spacing. Consider first the scattering problem in a given cell for some well defined energy (i.e., for fixed α). It is assumed that the potential function, $U_n(x)$, is symmetrical about the center of the cell and that it does not fill the cell, leaving regions of zero potential on either side. (x is the distance of a point in any cell from the center of that cell.) This description is illustrated in Figure 1, where the square well is used as an example. For fixed α , the solution of (I, 2) in the region of zero potential on the right is of the form

$$(I, 4) \quad \psi_R = a_+^n \exp i\alpha x + b_+^n \exp -i\alpha x,$$

and on the left it is of the form

$$(I, 5) \quad \psi_L = b_-^n \exp i\alpha x + a_-^n \exp -i\alpha x.$$

As seen in Figure 1 a_+ and a_- are the coefficients of outgoing waves, while b_+ and b_- are the coefficients of incoming waves. If a vector notation is introduced by

$$(I, 6) \quad \underline{a}^n = \begin{pmatrix} a_+^n \\ a_-^n \end{pmatrix}, \quad \underline{b}^n = \begin{pmatrix} b_+^n \\ b_-^n \end{pmatrix}$$

then the relation between these coefficients is given by a scattering matrix S_n :

$$(I, 7) \quad \underline{a}^n = S_n \underline{b}^n.$$

Figure 1 : A Typical Cell.

Since the potential is real, the scattering matrix is unitary:

$$(I, 8) \quad S_n^\dagger S_n = 1$$

where $S_n^\dagger$ is the transposed complex conjugate of S_n . From the symmetry of the potential it follows that the diagonal elements of S_n are identical. Using these relations, S_n may be expressed in terms of only two real parameters. If these are chosen to be the reflection coefficient r and the phase θ , the elements of S_n are given by

$$(I, 9) \quad \begin{aligned} S_{11} &= S_{22} = r \exp i\theta \\ \text{and} \\ S_{12} &= S_{21} = -i\sqrt{1-r^2} \exp i\theta. \end{aligned}$$

By rearranging equation (I, 7) a new matrix, M_n may be obtained that relates the coefficients of the waves running to the right and left respectively:

$$(I, 10) \quad \begin{pmatrix} a_+^n \\ b_+^n \end{pmatrix} = M_n \begin{pmatrix} b_-^n \\ a_-^n \end{pmatrix}.$$

The elements of M_n are given by

$$(I, 11) \quad \begin{aligned} M_{11} &= \bar{M}_{22} = \frac{-i \exp i\theta}{\sqrt{1-r^2}} \\ M_{12} &= \bar{M}_{21} = \frac{-ir}{\sqrt{1-r^2}}. \end{aligned}$$

The bar on M_{22} and M_{21} denotes the complex conjugate. Naturally, the r and θ will depend on the form of the n th potential function and on the energy.

To study propagation through the one-dimensional system, it is convenient to define a "transmission matrix," which relates the coefficients on the right of the n th cell to those on the right of the $(n-1)$ th cell. In addition, the relations appear more symmetrical if a new origin of coordinates is chosen on the boundary point of the cells (rather than at the center of each cell as before). Thus we define the vector

$$(I, 12) \quad \underline{e}_n = \begin{pmatrix} a_+^n \exp i \frac{\alpha d}{2} \\ b_+^n \exp - \frac{i \alpha d}{2} \end{pmatrix},$$

where the phase factors are due to the change in the origin of the coordinate systems in each cell. Inserting (I, 12) into (I, 10) then yields the transmission matrix R_n , which is defined by the relation

$$(I, 13) \quad \underline{e}_n = R_n \underline{e}_{n-1}.$$

The elements of R_n are given in terms of the elements of M_n by

$$(I, 14) \quad \begin{aligned} R_{11} &= \bar{R}_{22} = M_{11} \exp i \alpha d \\ R_{12} &= \bar{R}_{21} = M_{12} . \end{aligned}$$

By inserting the relations of (I, 10), it is seen that the determinant of this matrix is plus one and its trace is real.

In terms of the transmission matrices the problem of solving the differential equation (I, 2) with boundary conditions at one point for a given atomic arrangement is reduced to the evaluation of a matrix product. This may be seen in the following way: The choice of coefficients in the zeroth cell specifies the vector $\underline{e}_0$. The coefficients in any other cell are then given by

$$(I, 15) \quad \underline{e}_N = \prod_{n=N}^1 R_n \underline{e}_0 ,$$

where the form of R_n is completely specified by the potential function in the nth cell and by the energy.

For the case that all the potential wells are identical (i.e., the pure crystal) the problem of finding the propagating solutions is handled readily by the use of (I, 15). Since all of the R_n are equal, an $\underline{e}_0$ that is an eigenvector of one of them will be an eigenvector of the product. The eigenroots of any two by two matrix, C , are given by

$$(I, 16) \quad \lambda^2 - \text{trace } (C)\lambda + \det C = 0.$$

Since the determinant of the transmission matrix is one,

its eigenroots may be written in the form

$$(I, 17) \quad \begin{aligned} \lambda_+ &= \exp ikd \\ \lambda_- &= \exp -ikd \end{aligned} ,$$

where k is defined by

$$(I, 18) \quad \cos kd = \frac{\text{trace } R_n}{2} .$$

Inserting the eigenvectors $\underline{e}_0^+$ and $\underline{e}_0^-$ corresponding to the roots λ_+ and λ_- in (I, 14) we obtain:

$$(I, 19) \quad \begin{aligned} \frac{\underline{e}_N^+}{N} &= \frac{\underline{e}_0^+}{0} \exp iNkd \\ \frac{\underline{e}_N^-}{N} &= \frac{\underline{e}_0^-}{0} \exp -iNkd . \end{aligned}$$

These relations define two linearly independent solutions of (I, 2), and therefore the energy is doubly degenerate.

Equation (I, 19) is another way of stating Bloch's theorem (I, 1). From (I, 18) it is seen that the condition that must be satisfied in order that k be real is that $\text{trace } (R)$ must be less than two (that $\text{trace } (R)$ is real is assured by the fact that $R_{11} = \bar{R}_{22}$). Thus $k(E)$ is obtained by an investigation of the trace of the R matrix; the allowed bands occurring for energies for which $|\text{trace } (R)| \leq 2$ and the forbidden regions when $|\text{trace } (R)| > 2$.

For the Kronig-Penney case, the potential function of (I, 2) takes the form

$$(I, 20) \quad V(x) = -\frac{\hbar^2}{md} \sum_n V_n \delta(x - nd) .$$

The scattering matrix is given by

$$(I, 21) \quad S_n = \frac{1}{1 - i \frac{V_n}{ad}} \begin{pmatrix} \frac{iV_n}{ad} & 1 \\ 1 & \frac{iV_n}{ad} \end{pmatrix} ,$$

and the transmission matrix by

$$(I, 22) \quad R_n = \begin{pmatrix} (1 + \frac{iV_n}{ad}) \exp iad & \frac{iV_n}{ad} \\ -\frac{iV_n}{ad} & (1 - \frac{iV_n}{ad}) \exp -iad \end{pmatrix} .$$

If all of the potential strengths, V_n , in (I, 20) are equal to some constant which we shall call V (this is the case of a pure crystal), then from (I, 18) and (I, 22) it is seen that

$$(I, 23) \quad \cos kd = \cos ad - \frac{V}{ad} \sin ad .$$

This is known as the Kronig-Penney relation, and from it $k(E)$ for a pure crystal can be found.

In Figure 2, this relation is plotted as a function of the energy for a pure A crystal (specified by a potential strength V_A in each cell) and for a pure B crystal (specified by V_B). A random AB alloy can be formed by allowing the quantities V_n in (I, 20) to take on the values V_A and V_B in some random way. The Nordheim-Muto theory mentioned

Figure 2: The Energy Dependence of $\cos kd$.

earlier in this chapter predicts a relation for $k(E)$ which may be found for such an alloy by replacing V in (I, 23) with $\langle V \rangle$, which is defined by

$$(I, 24) \quad \langle V \rangle = C_A V_A + C_B V_B ,$$

where C_A and C_B are the concentrations of the A and B "atoms" respectively. A curve corresponding to this case is also shown in Figure 2. The values chosen for the calculation of these curves are $V_A = \pi$, $V_B = \pi/2$, and $C_A = C_B = 1/2$.

In order to put (I, 23) in a form more suitable for numerical computations, the substitution

$$(I, 25) \quad \pi v = \alpha d$$

is made. From the definition of α it can be seen that

$$(I, 26) \quad v^2 = 0.0268 d^2 E ,$$

where the lattice spacing, d , is measured in Angstrom units, and the energy of the electron, E , is measured in electron volts. For convenience we will choose a lattice spacing, d , such that

$$(I, 27) \quad v^2 = E .$$

The transition to a forbidden band occurs when the curves in Figure 2 cross the values plus or minus one. It

will be shown in Chapter IV that more detailed information about the density of allowed states can also be obtained from these curves.

Chapter II

THE DIRECT METHOD

The transmission matrices, R_m , furnish a method by which the coefficients of the plane wave solutions of the Schroedinger equation in any cell of a one-dimensional crystal can be found if the coefficients in a particular cell are given. As was pointed out in Chapter I, this approach is useful for obtaining a dispersion relation, $k(E)$, only for the simple case of a periodic potential. In this chapter the method will be generalized so that information can be obtained for the case in which the restriction of periodicity is relaxed.

We will consider an alloy consisting of equally spaced A and B atoms arranged in a random sequence. The concentrations, C_A and C_B , are considered to be fixed but arbitrary. In this infinite chain, any chosen sequence of a finite number of atoms with the proper concentration will occur. The procedure will be to determine the asymptotic behavior of certain properties of finite chains of A and B atoms (as the number of atoms approaches infinity) averaged over all possible chains that can be formed by permutation of the atoms. These average properties will then

be used to discuss the properties of the random alloy in which we are interested.

We first consider a particular arrangement of N atoms, of which $C_A N$ are of type A and $C_B N$ are of type B. Let the matrices A and B be the transmission matrices (for a given energy) for an A-cell (occupied by an A atom) and a B-cell respectively. Then the coefficients, $\underline{e}_N$, which characterize the state in the N th cell are given in terms of those in the 0th cell by the equation

$$(II, 1) \quad \underline{e}_N = AAB\dots BAB \underline{e}_0 = P_j \underline{e}_0.$$

The vector notation for the coefficients and also the matrices A and B are discussed in Chapter I (cf. equation (I, 13)). The matrix P_j stands for the particular product shown, the subscript serving to distinguish it from all of the other distinct products that may be formed by permutation of the A and B matrices.

We will now consider the average, $\langle P \rangle$, of the matrices P_j over all of these permutations. The matrix $\langle P \rangle$ has the property that applying it to any fixed state $\underline{e}_0$ in the 0th cell gives the average of all of the states in cell N . This may be written in the form of an equation

$$(II, 2) \quad \langle \underline{e}_N \rangle = \langle P \rangle \underline{e}_0,$$

where $\langle e_N \rangle$ is the average of the states in the final cell. Certain "pathological" cases are included in this averaging process (such as all of the A atoms being adjacent, or all of the B atoms being adjacent, etc.); however, the number of these is very small in comparison with the number of all possible permutations.

We expect that as N approaches infinity, $\langle P \rangle$ will take on an asymptotic form that will reflect the basic properties of the transmission matrix for an infinitely long random chain. This belief is based on the fact that the observable physical properties of a random alloy are not sensitive to the details of the atomic arrangement. Since the pathological cases mentioned above will have a very small weight in the average as the asymptotic limit is approached, it is plausible that $\langle P \rangle$ will have the expected properties. The results of a calculation that will be discussed at the end of this chapter justify this belief.

The scattering matrix for a given chain of N atoms can be obtained by solving (II, 1) for the coefficients of the waves progressing away from the ends of the chain (a_+^0 and a_-^N) in terms of the incoming waves (b_+^0 and b_-^N). It can be argued that the average of these scattering matrices over all permutations of the A and B atoms in the chain

(which we shall call $\langle S \rangle$) would be more useful than the matrix $\langle P \rangle$ that we have discussed. This is because $\langle S \rangle$ would yield the average of the outgoing waves when the incoming waves are specified, and this may be interpreted more readily than a formulation which requires that both the incoming and outgoing wave in the 0th cell must be specified. At the present time, however, there does not appear to be any way to find $\langle S \rangle$. It will be shown later that $\langle P \rangle$ will give essentially the same information as $\langle S \rangle$ if properly interpreted.

The matrix $\langle P \rangle$ can be found from the integral

$$(II, 3) \quad \langle P \rangle = \frac{C}{2\pi i} \oint \frac{(A+zB)^N dz}{z^{r+1}},$$

in which N is the number of atoms in the chains under consideration, $r = N C_B$ is the number of B atoms, and C is the reciprocal of the number of distinct products that can be formed by permutation of the r B atoms and $N-r$ A atoms (i.e., $C = (N-r)!r!/N!$). The path of integration must circle the origin one time. The integration has the effect of picking out the coefficient of z^r in the expansion of the N th power of $(A+zB)$, and this coefficient is the sum of all possible products that is desired.

The first step in evaluating the integral in (II, 3) is to find an expression for the N th power of $(A+zB)$. This may be accomplished by expressing the matrix in terms

of the Pauli spin matrices σ_x , σ_y , and σ_z .

The Pauli spin matrices are given by the following expressions:

$$\begin{aligned} \sigma_x &= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\ \sigma_y &= \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \\ \sigma_z &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} . \end{aligned} \tag{II, 4}$$

It can readily be shown by direct computation that

$$\sigma_x \sigma_y + \sigma_y \sigma_x = 0 \tag{II, 5}$$

for any permutation of the indices, and

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = I . \tag{II, 6}$$

These three matrices and the unit matrix form a complete set, and it follows that any two by two matrix can be expressed as a linear combination of them.

In terms of these matrices, $(A+zB)$ may be written in the form

$$(A+zB) = \Delta \left[(\cos p) I + \frac{i \mathbf{p} \cdot \boldsymbol{\sigma}}{p} \sin p \right] , \tag{II, 7}$$

where Δ and the three components of the vector $\underline{p}$ are determined by the elements of $(A+zB)$, p is the magnitude of $\underline{p}$, and $\underline{p} \cdot \underline{\sigma}$ is given by

$$(II, 8) \quad \underline{p} \cdot \underline{\sigma} = p_x \sigma_x + p_y \sigma_y + p_z \sigma_z .$$

It can be shown from equations (II, 5) and (II, 6) that

$$(II, 9) \quad (\underline{p} \cdot \underline{\sigma})^2 = p^2 I .$$

By taking the determinant of the matrix in (II, 7), it can be seen that

$$(II, 10) \quad \Delta^2 = \det (A+zB) .$$

Since the determinants of A and B are equal to one, Δ^2 can be written in the form

$$(II, 11) \quad \Delta^2 = 1 + \beta z + z^2 ,$$

where β is given in terms of the elements of A and B by

$$(II, 12) \quad \beta = A_{11} B_{22} + A_{22} B_{11} - A_{12} B_{21} - A_{21} B_{12} .$$

If we take the trace of the matrix in (II, 7) and use the definitions

$$(II, 13) \quad \begin{aligned} a &= \frac{\text{trace } A}{2} \\ b &= \frac{\text{trace } B}{2} , \end{aligned}$$

then the result may be put in the form

$$(II, 14) \quad \cos p = \frac{a+bz}{\Delta} .$$

Using the properties of the spin matrices that have been mentioned, equation (II, 7) can be re-expressed in the following way:

$$(II, 15) \quad (A+zB) = \Delta \exp i\mathbf{p} \cdot \underline{\sigma} .$$

Equation (II, 15) can be checked by expanding the exponential in a power series and using the relation (II, 9).

The right member of (II, 15) is now in a form such that the Nth power can be found by inspection. The result of this operation can be put in the form

$$(II, 16) \quad (A+zB)^N = \Delta^N \left[(\cos Np)I + \frac{i\mathbf{p} \cdot \underline{\sigma}}{p} \sin Np \right] .$$

From equation (II, 7), it can be shown that

$$(II, 17) \quad \frac{i\mathbf{p} \cdot \underline{\sigma}}{p} = \frac{(A+zB) - \Delta \cos pI}{\Delta \sin p} .$$

Inserting equation (II, 17) into (II, 16) yields an expression for the Nth power of (A+zB) as a linear combination of the A, B, and unit matrices. The same expression for the Nth power of (A+zB) can be obtained by using Sylvester's theorem, which is discussed on page 78 of reference 13.

The matrix $\langle P \rangle$ will now be found from the integral shown in equation (II, 3). Since the coefficients of the A, B, and unit matrices which appear in the expression for the Nth power of $(A+zB)$ are functions of z , the integration will be carried out on them. Thus, inserting (II, 17) into (II, 16) and the result into (II, 3), the following expression for $\langle P \rangle$ is obtained:

$$(II, 18) \quad \langle P \rangle = J_1(A-aI) + J_2(B-bI) + J_3I \quad .$$

The quantities a and b are defined in equations (II, 13), and J_1 , J_2 , and J_3 are given by the following contour integrals:

$$(II, 19) \quad \begin{aligned} J_1 &= \frac{C}{2\pi i} \oint \frac{\Delta^{N-1} \sin Np}{z^{r+1} \sin p} dz \\ J_2 &= \frac{C}{2\pi i} \oint \frac{\Delta^{N-1} \sin Np}{z^r \sin p} dz \\ J_3 &= \frac{C}{2\pi i} \oint \frac{\Delta^N \cos Np}{z^{r+1}} dz \quad . \end{aligned}$$

The functions p and Δ are given in equations (II, 11) and (II, 14), and the other quantities that appear in (II, 19) were defined in connection with (II, 3).

Since the determinants of the matrices A and B are equal to one, equation (II, 18) can be used to show that the determinant of $\langle P \rangle$ is given by the relation.

$$(II, 20) \quad \det \langle P \rangle = J_3^2 - (J_1 a + J_2 b)^2 \\ + (J_1^2 + J_2^2 + \beta J_1 J_2) \quad ,$$

where β is defined in equation (II, 12). The trace of $\langle P \rangle$ is given by the relation

$$(II, 21) \quad \text{trace} \langle P \rangle = 2J_3 \quad .$$

From equation (I, 16), which gives the characteristic equation for any two by two matrix, it can be seen that the eigenroots of $\langle P \rangle$, Λ_1 and Λ_2 , satisfy the following equations:

$$(II, 22) \quad \Lambda_1 \Lambda_2 = \det \langle P \rangle \\ \Lambda_1 + \Lambda_2 = \text{trace} \langle P \rangle \quad .$$

Using equations (II, 18) through (II,22), the calculation of the asymptotic form of $\langle P \rangle$ will now be carried through for the special case that the potentials have the form of δ -functions. This case is relatively simple because β (cf. equation (II, 12)) is equal to two, and is thus independent of the strength of the potentials and independent of the energy. The fact that $\beta = 2$ can easily be shown from the form of the matrices A and B which are given for this case by equation (I, 22).

For the determination of the eigenroots of $\langle P \rangle$, we must now evaluate:

$$\begin{aligned}
 \det \langle P \rangle = & \left[\frac{C}{2\pi i} \oint \frac{(1+z)^N \cos Np}{z^{r+1}} dz \right]^2 \\
 (II, 23) \quad & - \left[\frac{C}{2\pi i} \oint \frac{(1+z)^N \sin Np \cos p}{z^{r+1} \sin p} dz \right]^2 \\
 & + \left[\frac{C}{2\pi i} \oint \frac{(1+z)^N \sin Np}{z^{r+1} \sin p} dz \right]^2
 \end{aligned}$$

and

$$(II, 24) \quad \frac{\text{trace } \langle P \rangle}{2} = \frac{C}{2\pi i} \oint \frac{(1+z)^N \cos Np}{z^{r+1}} dz,$$

where

$$(II, 25) \quad \cos p = \frac{a + bz}{1 + z}.$$

These expressions are obtained from equations (II, 19) through (II, 21) by setting $\beta = 2$ in the definitions (II, 11) and (II, 14).

The integrals in (II, 23) and (II, 24) will now be evaluated by the saddle point method. This method, which is discussed in reference 1, yields an asymptotic expression for the contour integral of a function of the form $\exp Nf(z)$ in the limit as N approaches infinity. In applying this method, it is necessary to deform the path of integration, Γ , so that there is very little contribution

to the value of the integral over the entire path except in the immediate neighborhood of one or more points on the path where practically the entire contribution takes place. It is shown in reference 1 that this can be accomplished by deforming Γ so that it passes through certain of the saddle points, z' , of $f(z)$ along the line of steepest descent and otherwise remains in regions of the z plane for which $\text{Re } f(z) < \text{Re } f(z')$. The major contribution to the integral then comes from the neighborhood of these saddle points. The saddle points of $f(z)$ are the roots of the equation

$$(II, 26) \quad \frac{df}{dz} = 0 ,$$

and may be recognized on a contour map of $\text{Re } f(z)$ as the points at which that function has a mini.-max. (i.e., the points at which the function has a minimum along one path in the z plane and a maximum along another). The choice of the saddle points that must be used for the evaluation of a given integral will depend on the path of integration that is specified for that integral.

It is found in applying the saddle point method to the integrals in (II, 23) and (II, 24) that all of them can be evaluated by investigating two basic integrals of the form

$$\begin{aligned}
 K_- &= \frac{C}{2\pi i} \oint \frac{(1+z)^N \exp -iNp}{z^{r+1}} dz \quad , \\
 (II, 27) \quad K_+ &= \frac{C}{2\pi i} \oint \frac{(1+z)^N \exp iNp}{z^{r+1}} dz \quad .
 \end{aligned}$$

This is true because the functions $\cot p$ and $1/\sin p$ are slowly varying in the neighborhood of the saddle points of the above integrals and may be taken outside of the integral sign and replaced with their value at the saddle point. All of the integrands in (II, 23) and (II, 24) can be generated by adding and subtracting products of the above-mentioned functions with the integrands in (II, 27). The assertion that the functions are slowly varying in the neighborhood of the saddle points would not be true if a saddle point coincided with a point for which $\sin p = 0$. The points at which $\sin p = 0$ are branch points of the integrands, however, and it will be seen that the saddle points stay away from these.

After the integrals in (II, 23) have been evaluated, it will be convenient to have on hand an asymptotic expression for $1/C$. The quantity $1/C$ is a binomial coefficient, which may be expressed as a contour integral in the following way:

$$(II, 28) \quad 1/C = \binom{N}{r} = \frac{1}{2\pi i} \oint \frac{(1+z)^N}{z^{r+1}} dz.$$

The saddle point method will be used to evaluate this integral, and it will be seen that the information obtained in carrying out this operation will be of use in the investigation of the more complicated integrals of equations (II, 27).

The expression (II, 28) can be put into a form suitable for application of the saddle point method by defining

$$(II, 29) \quad 1/C = \frac{1}{2\pi i} \oint \exp Ng(z) dz ,$$

where

$$(II, 30) \quad g(z) = \ln(1+z) - \frac{r+1}{N} \ln z .$$

The saddle points of the integral in (II, 29) are given by the roots of

$$(II, 31) \quad \frac{dg(z)}{dz} = 0 ,$$

There is only one root of this equation and hence one saddle point, which is given by

$$(II, 32) \quad z_0 = \frac{r+1}{N-r-1} \doteq \frac{C_B}{1-C_B} ,$$

(since $C_B = r/N$). The integral can now be expressed in terms of $g(z_0)$ and $g''(z_0)$ (cf. reference 1, equation 4.6.13), as follows:

$$(II, 33) \quad 1/C = \frac{\exp Ng(z_0)}{2\pi Ng''(z_0)} .$$

In Figure 3, a contour map of $\operatorname{Re} g(z)$ is shown for the case $C_B = 1/2$. The function approaches infinity at the origin and as $|z|$ approaches infinity, and it approaches minus infinity at $z = -1$. The path of integration is shown as a dotted line in Figure 3, and the saddle point is indicated by a dot.

We will now investigate the integral K_- which is given in equation (II, 27). The expression for K_- can be written in a form suitable for the application of the saddle point method in the following way:

$$(II, 34) \quad K_- = \frac{C}{2\pi i} \oint \exp Nh_-(z) ,$$

where

$$(II, 35) \quad h_-(z) = -ip(z) + g(z) .$$

The function $g(z)$ used in (II, 35) is defined in (II, 30). The function $h_-(z)$ is not single-valued because $p(z)$ is defined as an arc cosine (cf. equation (II, 25)). It can be made single-valued by choosing a Riemann sheet and introducing a branch cut. The sheet that is chosen is the one for which $0 < \operatorname{Re} p(z) < \pi$, and the branch cut is taken along the real axis on the line between the branch points

Figure 3 : The Contour Map of $\text{Re } g(z)$.

given by $\cos p = 1$ and $\cos p = -1$ for which $\operatorname{Re} p(z)$ takes the value 0 or π .

The saddle points of $h_-(z)$ are given by the roots of the equation

$$(II, 36) \quad \frac{dh_-(z)}{dz} = 0$$

Inserting the expression for $h_-(z)$ from (II, 35) into (II, 36) and multiplying the result by $(1+z)^2 z \sin p$ yields

$$(II, 37) \quad [C_B - (1-C_B)z] (1+z) \sin p = -1(a-b)z .$$

(Actually $(r+1)/N$ occurs in the above equation in place of C_B , but the difference between the two is of no importance in the limit as N approaches infinity.) By direct substitution it is seen that $z = -1$ is a solution of (II,37). A closer inspection shows that this is not a root of (II,36) and appears only as a result of transforming the equation into the form shown in (II, 37).

The other roots of (II, 37) can be found by squaring both sides of the equation and factoring out $(1+z)$. This leads to the following cubic equation:

$$(II, 38) \quad \begin{aligned} z^3 &+ \left[\frac{1-2ab+b^2}{1-b^2} - 2z_0 \right] z^2 \\ &+ \left[\left(\frac{1-2ab+a^2}{1-b^2} \right) z_0^2 - 2 \left(\frac{1-a^2}{1-b^2} \right) z_0 \right] z \\ &+ \left(\frac{1-a^2}{1-b^2} \right) z_0^2 = 0 , \end{aligned}$$

where z_0 is given in equation (II, 32). The roots of equation (II, 38) vary with the energy of the electron (through the energy dependence of a and b) and with the concentration (through the dependence of z_0 on C_P).

Since (II, 38) was obtained by a series of transformations on (II, 36), it is necessary to investigate the real part of $h_-(z)$ in order to see which roots of that equation actually correspond to saddle points of $h_-(z)$. Such an investigation will also show which saddle points must be considered in the evaluation of the integral K_- . From (II, 35) it can be seen that the real part of $h_-(z)$ is given by

$$(II, 39) \quad \operatorname{Re} h_-(z) = \operatorname{Im} p(z) + \operatorname{Re} g(z).$$

An investigation of $\operatorname{Re} h_-(z)$ which will be described later shows the following: If the cubic equation (II, 38) has one real root and two complex conjugate roots, then the real root and the complex root in the upper half-plane are saddle points of $h_-(z)$, but the real root is not needed in the evaluation of K_- . If (II, 38) has three real roots, then all three of these roots are saddle points of $h_-(z)$. However, only one of them is needed for the evaluation of K_- .

The integral K_+ , which is given in (II, 27), can be investigated in a manner analogous to that used for the

investigation of K_- . It is first put into the form

$$(II, 40) \quad K_+ = \frac{C}{2\pi i} \oint \exp N h_+(z) ,$$

by defining

$$(II, 41) \quad h_+(z) = ip(z) + g(z) .$$

The Riemann sheet chosen to make $p(z)$ single-valued was discussed in connection with equation (II, 35).

By carrying out on $h_+(z)$ the operations which led to equations (II, 36) through (II, 38), it can be shown that the saddle points of $h_+(z)$ are also roots of (II, 38). The reason for this is found from an investigation of the real part of $h_+(z)$. From (II, 41) it can be seen that

$$(II, 42) \quad \operatorname{Re} h_+(z) = -\operatorname{Im} p(z) + \operatorname{Re} g(z) .$$

Now, from the defining equations (II, 25) and (II, 30), it can be shown that on the Riemann sheet chosen $p(z)$ and $g(z)$ are such that the real part of $g(z)$ is symmetric under reflection through the real axis, while the imaginary part of $p(z)$ is antisymmetric under this operation. A comparison of (II, 39) and (II, 42) shows that the only difference between $\operatorname{Re} h_+(z)$ and $\operatorname{Re} h_-(z)$ is in the sign of $\operatorname{Im} p(z)$. Therefore, the function $\operatorname{Re} h_+(z)$ is obtained from the function $\operatorname{Re} h_-(z)$ by reflecting it through the real axis.

When the cubic equation (II, 38) has one real and two complex conjugate roots it has been pointed out that the saddle point needed for the evaluation of K_- is given by the complex root in the upper half-plane. From the symmetry between $\operatorname{Re} h_+(z)$ and $\operatorname{Re} h_-(z)$ that we have discussed, it follows that the saddle point needed for the evaluation of K_+ is given by the complex conjugate root in the lower half-plane. When (II, 38) has three real roots, all of these are saddle points of $h_+(z)$. As was the case for K_- , however, only one of them is needed for the evaluation of K_+ .

Before making a detailed investigation of the saddle points of K_+ and K_- , we will discuss the general properties of $\langle P \rangle$ for the case that (II, 38) has one real and two complex conjugate roots (which we shall call Case 1) and for the case that it has three real roots (which we shall call Case 2).

Case 1: (Equation (II, 38) has one real and two complex conjugate roots.)

The symbol z_1 will denote the saddle point of $h_-(z)$ in the upper half-plane. The integral K_- can be expressed in terms of $h_-(z_1)$ and $h_-''(z_1)$ in the following way (cf. equation 4.6.13 in reference 1):

$$(II, 43) \quad K_- = \frac{C}{\sqrt{2\pi N h_-''(z_1)}} \exp N h_-(z_1) \quad .$$

Inserting the asymptotic expression for $1/C$ from (II, 33) into (II, 43) yields

$$(II, 44) \quad K_- = \frac{\sqrt{g''(z_0)}}{\sqrt{h''(z_1)}} \exp N [h_-(z_1) - g(z_0)].$$

This expression is complex. Since the saddle point of $h_+(z)$ is the complex conjugate of z_1 , it can be shown that the asymptotic expression for K_+ is given by the complex conjugate of the expression in (II, 41). Writing this in the form of an equation we have

$$(II, 45) \quad K_+ = \bar{K}_-.$$

Using equations (II, 44) and (II, 45) in equations (II, 23) and (II, 24) yields expressions for $\det \langle P \rangle$ and $\text{trace} \langle P \rangle$. These expressions may be written in the form

$$(II, 46) \quad \det \langle P \rangle = |K_-|^2 \frac{\sin^2[\text{Re } p]}{|\sin p|^2},$$

and

$$(II, 47) \quad \text{trace} \langle P \rangle = K_+ + K_- ,$$

where p is evaluated at $z = z_1$. These expressions are both real. The eigenroots of $\langle P \rangle$, Λ_1 , and Λ_2 , can be found from equation (II, 22) by using equations (II, 46) and (II, 47). They may be written in the following form:

$$\begin{aligned}
 \Lambda_1 &= \exp N(\gamma + i\theta) \\
 \Lambda_2 &= \exp N(\gamma - i\theta) ,
 \end{aligned}
 \tag{II, 48}$$

where

$$\begin{aligned}
 \exp N\gamma &= \frac{\sin [\operatorname{Re} p]}{|\sin p|} \left| \frac{\sqrt{g''(z_0)}}{\sqrt{h''(z_1)}} \right| \\
 &\times \exp N \left[\operatorname{Re} h_-(z_1) - \operatorname{Re} g(z_0) \right]
 \end{aligned}
 \tag{II, 49}$$

and

$$\cos N\theta = \frac{|\sin p|}{\sin [\operatorname{Re} p]} \cos N \left[\operatorname{Re} p(z_1) + \phi_1 - C_B \phi_2 \right].
 \tag{II, 50}$$

The quantities ϕ_1 and ϕ_2 which enter into equation (II, 50) are given by

$$\begin{aligned}
 \phi_1 &= \arg(1+z_1) \\
 \phi_2 &= \arg z_1
 \end{aligned}
 \tag{II, 51}$$

By taking the logarithm of (II, 49) it can be shown that

$$\gamma = \operatorname{Re} h_-(z_1) - \operatorname{Re} g(z_0) ,
 \tag{II, 52}$$

to within an error that is of the order of $1/N$. The detailed investigation of the saddle points which is discussed at the end of this chapter shows that γ is always positive.

We will now investigate equation (II, 50). The function $|\sin p|/\sin [\operatorname{Re} p]$ is always greater in absolute

magnitude than one, and it is positive on the Riemann sheet that we are using. Thus, when $\text{Re } p + \phi_1 - C_B \phi_2$ varies smoothly over a given interval, θ will vary in a similar way with the exception that it will become imaginary in certain intervals whose width is of the order of $1/N$. Since these intervals may be ignored in the limit as N approaches infinity, we write

$$(II, 53) \quad \theta = \text{Re } p + \phi_1 - C_B \phi_2$$

to within an error that is of the order of $1/N$.

For Case 1, the eigenroots of $\langle P \rangle$ take on a physical meaning in the following way. Suppose $\underline{e}_+$ is the eigenvector of $\langle P \rangle$ such that

$$(II, 54) \quad \langle P \rangle \underline{e}_+ = \underline{e}_+ \exp N(\gamma + i\theta) .$$

Operating on $\underline{e}_+$ with any of the transmission matrices, P_j (cf. equation (II, 1)) yields

$$(II, 55) \quad P_j \underline{e}_+ = \underline{e}_+^j \exp iN\phi_j ,$$

where the over-all phase has been factored out and shown explicitly. The quantity ϕ_j is the average phase change per unit cell in the chain under consideration. Using the property of $\langle P \rangle$ expressed in equation (II, 2), the average of the states in the N th cell may be written in the form

$$(II, 56) \quad \langle \underline{e}_+^j \exp iN\phi_j \rangle = \underline{e}_+ \exp N(\gamma+i\theta) .$$

Factoring out the mean of the ϕ_j over all of the chains, $\langle \phi \rangle$, (II, 56) may be rewritten in the form

$$(II, 57) \quad \langle \underline{e}_+^j \exp iN(\phi_j - \langle \phi \rangle) \rangle \exp iN\langle \phi \rangle = \underline{e}_+ \exp N(\gamma+i\theta) .$$

If we assume that the fluctuations in the quantities $\underline{e}_+^j$ are uncorrelated with the fluctuations of ϕ_j about $\langle \phi \rangle$, the average in the left member of (II, 57) can be split in the following way:

$$(II, 58) \quad \langle \underline{e}_+^j \exp iN(\phi_j - \langle \phi \rangle) \rangle = \langle \underline{e}_+^j \rangle \langle \exp iN(\phi_j - \langle \phi \rangle) \rangle .$$

If we further assume that the phase fluctuations, $(\phi_j - \langle \phi \rangle)$, can be described by a Gaussian distribution with variance σ , it can be shown that

$$(II, 59) \quad \langle \exp iN(\phi_j - \langle \phi \rangle) \rangle = \exp - \frac{\sigma^2 N^2}{2} .$$

The coefficients in the Nth cell, which are given (except for their over-all phase) by $\underline{e}_+^j$, may become large or small. In taking an average, the large ones will predominate. We assume that as N approaches infinity, a finite constant G which is independent of N can be defined such that

$$(II, 60) \quad \langle \underline{e}_+^j \rangle = \underline{e}_+ \exp GN .$$

From equation (II, 57), it can be seen that

$$(II, 61) \quad \theta = \langle \phi \rangle .$$

Using equations (II, 57) through (II, 60), it can be shown that

$$(II, 62) \quad \gamma = G - \frac{\sigma^2}{2} N .$$

If γ is bounded and independent of N as N approaches infinity, then σ must be given by

$$(II, 63) \quad \sigma = \frac{s}{\sqrt{N}}$$

where s is independent of N . Substituting (II, 63) into (II, 62) yields

$$(II, 64) \quad \gamma = G - \frac{s^2}{2} .$$

It is felt that the assumptions made in this paragraph are plausible, and they are borne out by a calculation described at the end of this chapter which gives results that are physically meaningful. The interpretation that we are led to is that θ must be the mean of the average phase change per unit cell in each chain, ϕ_j and that the distribution of the ϕ_j about θ will be very narrow. The quantity θ is the analogue for the random alloy of the phase change per unit cell for a pure crystal, k_d , given by equation (I, 18). The quantity γ gives information about the way in which the magnitudes of the coefficients

behave, and about the distribution of the phases.

The quantity γ can be interpreted to some extent by considering the average scattering matrix $\langle S \rangle$ that was discussed previously. It was pointed out that the advantage of the matrix $\langle S \rangle$ was that the average outgoing waves could be found if the incoming waves were specified. In particular we could consider a problem in which there is only one incoming wave (specified by the coefficient a_0) and calculate the average of the waves that are transmitted through the crystal. We shall attempt to find the same information using the transmission matrices.

In terms of the transmission matrix for a given chain, P_j , we can write (cf. equation (II, 1))

$$(II, 65) \quad \begin{pmatrix} a_N \\ 0 \end{pmatrix} = P_j \begin{pmatrix} a_0 \\ b_0 \end{pmatrix},$$

where a_0 and b_0 are the coefficients of the incoming and reflected wave respectively, and a_N is the coefficient of the transmitted wave. The determinant of P_j is one, since it is the product of matrices with this property. Using this fact, it can easily be shown that

$$(II, 66) \quad a_N = \frac{a_0}{(P_j)_{22}}.$$

If we now take the average of both members of this equation the average of the coefficients of the transmitted

waves, $\langle a_N \rangle$, is given by

$$(II, 67) \quad \langle a_N \rangle = \left\langle \frac{1}{(P_j)_{22}} \right\rangle a_0 .$$

In general the average of the reciprocal of a quantity is not equal to the reciprocal of the average, but if it is assumed that this substitution can be used as an approximation we are led to the following result: Since the quantity γ is positive, the elements of $\langle P \rangle$ increase exponentially with increasing N . Keeping the coefficient of the incoming wave fixed, it is seen that the transmitted waves will be damped on the average. Thus, in this approximation, the quantity γ can be interpreted as a damping factor.

For Case 1, θ is always real, and this corresponds to an allowed zone for the random alloy.

Case 2: (Equation (II, 38) has three real roots)

The symbol z_2 will denote the real saddle point of $h_-(z)$, and z_3 will denote the real saddle point of $h_+(z)$. The asymptotic expressions for K_- and K_+ take the following form for this case:

$$(II, 68) \quad K_- = \frac{\sqrt{g''(z_0)}}{\sqrt{h_-''(z_2)}} \exp N [h_-(z_2) - g(z_0)]$$

and

$$(II, 69) \quad K_+ = \frac{\sqrt{g''(z_0)}}{\sqrt{h_+''(z_3)}} \exp N [h_+(z_3) - g(z_0)] .$$

It will be shown during the course of the detailed investigation of the saddle points that the function $p(z)$ which appears in the definitions of $h_+(z)$ and $h_-(z)$ is pure imaginary or such that $p(z) - \pi$ is pure imaginary when evaluated at z_2 and z_3 . In either case it can be shown that the asymptotic expressions for K_+ and K_- given by equations (II, 68) and (II, 69) are real. The trace and determinant of $\langle P \rangle$ for this case can be found by using equations (II, 68) and (II, 69) in equations (II, 23) and (II, 24). The eigenroots of $\langle P \rangle$ can then be found from (II, 22). If these operations are carried out it can be seen that the eigenroots of $\langle P \rangle$ are real. From the physical interpretation of the eigenroots of $\langle P \rangle$ given in the previous paragraph we see that this corresponds to a forbidden zone of the random alloy.

The behavior of the solutions in a forbidden zone are of no interest for a discussion of the band structure of a crystal. Therefore, we will only investigate the saddle points for Case 2 to the extent necessary to justify the statements made in this paragraph.

We will now investigate the saddle points of $h_-(z)$ and $h_+(z)$ in detail. It has been pointed out that the roots of (II, 38) depend on the energy of the electron

and on the concentration C_B (for a given choice of potential strengths V_A and V_B). The energy dependence of the roots is due to the energy dependence of the quantities a and b , and a comparison of equations (II, 13) and (I, 18) shows that these quantities are the cosines of kd for a pure A crystal and a pure B crystal respectively. In Figure 2 they are plotted as a function of the energy for the choice of potential strengths $V_A = \pi$ and $V_B = \pi/2$.

It can be seen from Figure 2 that the variation of a and b with the energy can be divided into the following energy zones: (1) the doubly allowed zone for which $|a| \leq 1$ and $|b| \leq 1$; (2) the singly allowed zone for which $|a| > 1$ while $|b| \leq 1$, or $|b| > 1$ while $|a| \leq 1$; (3) the doubly forbidden zone for which $|a| > 1$ and $|b| > 1$. It is convenient to discuss the saddle points for each of these zones individually.

In the doubly allowed zone, (II, 38) has one real root and two complex conjugate roots for any value of C_B . A contour map of $\text{Im } p(z)$ (cf. equation (II, 25)) for typical values of a and b in this zone is shown in Figure 4. The branch points are marked with crosses and the branch cut is shown as a heavy line. The function approaches infinity at $z = -1$ on the upper side of the branch cut and minus infinity at $z = -1$ on the lower side of the branch cut. It approaches zero as $|z|$ approaches

Figure 4 : The Contour Map of $\text{Im } p(z)$ for the Doubly Allowed Zone.

infinity. The function $\text{Re } h_-(z)$ is obtained by adding $\text{Im } p$ to $\text{Re } g(z)$ (cf. equation (II, 39)). The function $\text{Re } g(z)$ for $C_B = 1/2$ is shown in Figure 3. The contour map for $\text{Re } h_-(z)$ for this zone is shown in Figure 5. The branch cut and branch points are marked as in Figure 4 and the saddle points are shown by dots. The path of integration is shown by a dotted line. The function approaches infinity at the origin and as $|z|$ approaches infinity, and it approaches minus infinity at $z = -1$ on the lower side of the branch cut.

It can be seen from Figure 5 that the path of integration can be chosen such that it circles the origin once and passes through the saddle point, z_1 , in the upper half-plane without passing through any regions of the z plane for which $\text{Re } h_-(z) > \text{Re } h_-(z_1)$. Thus, the real saddle point does not need to be used for the evaluation of K_- .

In the singly allowed zone, (II, 38) has one real root and two complex conjugate roots for energies below a certain critical energy E_c . For energies above E_c (II, 38) has three real roots. The critical energy depends on the concentration C_B , and can be found from an investigation of the discriminant of (II, 38).

In Figure 6, the contour map of $\text{Im } p(z)$ for $E < E_c$ is shown, and the corresponding contour map for $\text{Re } h_-(z)$ is shown in Figure 7. The function $\text{Re } h_-(z)$ has the same

Figure 5 : The Contour Map of $\text{Re } h_1(z)$ for the Doubly Allowed Zone.

Figure 6 : The Contour Map of $\text{Im } p(z)$ for the Singly Allowed Zone, $E < E_c$.

Figure 7: The Contour Map of $\text{Re } h_-(z)$ for the Singly Allowed Zone, $E < E_c$.

general behavior for this case as it had in the doubly allowed zone. It can be seen from Figure 7 that the real saddle point is not needed in the evaluation of K_- for the same reason that was given in the discussion of the doubly allowed zone. The functions $\text{Im } p(z)$ and $\text{Re } h_-(z)$ for $E > E_c$ are shown in Figures 8 and 9 respectively. The path of integration used for the evaluation of K_- and that used for the evaluation of K_+ are discussed in the next paragraph.

In the doubly forbidden zone, (II, 38) has three real roots for any concentration C_B . The contour maps of $\text{Im } p(z)$ and $\text{Re } h_-(z)$ for this zone are shown in Figures 10 and 11. For energies in this zone the Riemann sheet and branch cut that we have been using are no longer convenient for the evaluation of K_- . A new sheet is now chosen which corresponds to $-\pi < \text{Re } p < \pi$ and $\text{Im } p \geq 0$. The branch cut is taken along the real axis on the line between the branch points given by $\cos p = 1$ and $\cos p = -1$ for which $\text{Im } p(z) = 0$. With this choice of a Riemann sheet, the function $\text{Re } h_+(z)$ can not be obtained from $\text{Re } h_-(z)$ by reflecting the latter through the real axis.

The contour maps for $\text{Re } h_-(z)$ and $\text{Re } h_+(z)$ are shown in Figures 12 and 13 for the new choice of a Riemann sheet. It can be seen that the path of integration of $h_-(z)$ passes through the saddle point, z_2 , without

Figure 8 : The Contour Map of $\text{Im } p(z)$ for the Singly Allowed Zone, $E > E_c$.

Figure 9 : The Contour Map of $\text{Re } h_1(z)$ for the Singly Allowed Zone, $E > E_c$.

Figure 10: The Contour Map of $\text{Im } p(z)$ for the Doubly Forbidden Zone.

Figure 11 : The Contour Map of $\text{Re } h_1(z)$ for the Doubly Forbidden Zone.

Figure 12: The Contour Map of $\text{Re } h_1(z)$ for the Doubly Forbidden Zone (New Riemann Sheet)

Figure 13: The Contour Map of $\text{Re } h_+(z)$ for the Doubly Forbidden Zone (New Riemann Sheet).

passing through any regions of the z plane for which $\operatorname{Re} h_-(z) > \operatorname{Re} h_-(z_2)$. In a like manner, the path of integration of $h_+(z)$ passes through the saddle point z_3 without passing through any regions for which $\operatorname{Re} h_+(z) > \operatorname{Re} h_+(z_3)$. Therefore, the only saddle point needed for the evaluation of K_- is z_2 , and the only one needed for the evaluation of K_+ is z_3 . A similar result can be obtained for the part of the singly allowed zone for which $E > E_c$.

From Figures 9 and 11 it can be seen that the real saddle points always occur on the real axis and on our original branch cut. An investigation of the function $p(z)$ shows that $p(z)$ or $p(z) - \pi$ is purely imaginary on this cut. This justifies the statement made in the discussion of Case 2.

The discussion of the saddle points that has been given shows that the doubly allowed zones and the part of the singly allowed zones for which $E < E_c$ correspond to allowed zones for the random alloy. The path of integration for these zones cross the positive real axis at some point, z' , that is not on the branch cut. At such a point, it can be seen from Figures 4 and 6 that $\operatorname{Im}(p) = 0$, so that

$$(II, 70) \quad \operatorname{Re} h_-(z') = \operatorname{Re} g(z') .$$

From the criterion for the choice of the proper path of integration, the following inequality must hold:

$$(II, 71) \quad \operatorname{Re} h_-(z_1) > \operatorname{Re} h_-(z') ,$$

where z_1 is the saddle point of $h_-(z)$. It can be seen from Figure 3 that $\operatorname{Re} g(z)$ has a minimum on the positive real axis at the saddle point z_0 , so that the inequality

$$(II, 72) \quad \operatorname{Re} g(z') \geq \operatorname{Re} g(z_0)$$

will hold if z' is any point on the positive real axis. It follows from the expressions (II, 70) through (II, 72) that

$$(II, 73) \quad \operatorname{Re} h_-(z_1) > \operatorname{Re} g(z_0) .$$

Using this inequality in equation (II, 52) demonstrates the result that γ is always positive in the allowed zones of the random alloy.

For a particular choice of potential strengths V_A and V_B and concentration C_B , the saddle points can be calculated from equation (II, 38) for various energies. By inserting the results of such a calculation in equations (II, 52) and (II, 53), enough values for θ and γ can be found that these quantities can be plotted as smoothly varying functions of the energy. The results of this calculation for the choice $V_A = \pi$, $V_B = \pi/2$, and $C_A = C_B = 1/2$ are shown in Figures 14 and 15.

The cosine of θ is shown in Figure 14 and compared with $\cos kd$ obtained from the Nordheim-Muto theory

Figure 14: The Energy Dependence of $\cos \theta$.

Figure 15: The Energy Dependence of Y .

(cf. equation (I, 22) and (I, 23)) for the same choice of V_A , V_B , and C_B . The quantity γ is shown in Figure 15.

It should be pointed out that the calculations shown in Figures 14 and 15 were carried out on a desk computer, and it was impossible to plot as many points in the negative energy regions (where the functions a and b vary rapidly) as might be desired. This leads to no difficulty in plotting $\cos \theta$ because the form of the function can be obtained from general considerations about the behavior of the saddle points. The quantity γ cannot be specified very completely by such considerations, however, and in the allowed zones of lowest energy only the general range of values may be specified.

No values are plotted for the forbidden zones of the random alloy because the details of the behavior of the solutions in these regions are not of interest as was mentioned in the discussion of Case 2. No calculations are shown for energies such that $E > 4$ because the results shown for the region $1 < E < 4$ are typical for the allowed zones at higher energies.

From Figure 14 it can be seen that $\cos \theta$ is very nearly equal to the Nordheim-Muto prediction (shown by the dotted line) in the energy region $1 < E < 4$. The difference between the two is of interest, however, as will be shown in Chapter IV.

The allowed zone for the negative energy region predicted by the Nordheim-Muto theory is split into two in our work. They are separated by a forbidden zone which is bounded by two critical energies that we shall call E_1 and E_2 (E_1 being the lower bound and E_2 being the upper). An investigation of the variation of the saddle points with the energy shows that in general θ will be given by

$$(II, 74) \quad \theta_c = C_A \pi + \pi ,$$

at E_1 and E_2 . This comes about because the saddle points approach a point on the real axis, z_c , which is less than minus one as the energy approaches E_2 from the positive side and E_1 from the negative side. As has been pointed out, the saddle points on the real axis appear on the branch cut and on this section of the cut $\text{Re } p(z) = \pi$. Thus, as the saddle points approach z_c , ϕ_1 and ϕ_2 (cf. equation (II, 51)) approach π and $\text{Re } p(z)$ approaches π . Inserting these values in equation (II, 53) yields the expression (II, 74). This effect does not appear at the other boundaries of the zones because the saddle points approach the positive real axis, and it follows that ϕ_1 and ϕ_2 approach zero. Equation (II, 74) is of interest in the discussion of the density of states for the random alloy as will be shown in Chapter IV.

The extension of this work to potentials which do not take the form of δ -functions is straight-forward in principle. The equation for $\langle P \rangle$ given in (II, 18) is quite general, but the evaluation of the integrals by the saddle point method is complicated by the fact that saddle points must be obtained from the roots of a sixth degree equation. If this complication were overcome, however, it is to be expected that results could be obtained that are analogous to the ones that we have shown here for the case of δ -function potentials.

Chapter III

THE INTUITIVE METHOD

The material in this chapter consists of a specialization of the work of Korringa⁶ on the three-dimensional random alloy (cf. Chapter I) to the one-dimensional case. The aim of the method is to find an average scattering matrix for any cell of the random alloy rather than an average potential as is done in the Nordheim-Muto theory. It will be seen that the one-dimensional topology and the use of fixed potentials in each cell that do not overlap into adjacent cells make the problem simple to formulate, but some of the crucial assumptions that are made in the three-dimensional problem become less plausible for this case. It is of interest to carry through the work for this case, however, and compare the results with the predictions of the direct method given in Chapter II.

We will consider a one-dimensional random alloy consisting of equally spaced A and B atoms in a random sequence with fixed (but arbitrary) concentrations C_A and C_B . The Schroedinger equation for this problem is obtained from equation (I, 2) by specifying that the potential function, $U_n(x)$, will take on the form $U_A(x)$ in an A-cell (i.e. a cell that contains an A atom) and $U_B(x)$ in a B-cell.

It is shown in Chapter I that the solution of the Schroedinger equation (I, 2) can be characterized by specifying the coefficients of the plane wave solutions in the region of zero potential in each cell (cf. equations (I, 4) and (I, 5), and Figure 1. The coefficients of the outgoing waves traveling from the nth lattice point to the right and the left (a_+^n and a_-^n) are related to the incoming waves (b_+^n and b_-^n) by the scattering matrix for the nth cell, S_n . Using the vector notation for the coefficients introduced in Chapter I (cf. equation (I, 6), we can write

$$(III, 1) \quad \underline{a}^n = S_n \underline{b}^n$$

(This equation appears in Chapter I as (I, 7)). The matrix S_n is completely specified by the potential in the nth cell and by the energy of the electron. If cell n contains an A atom, S_n is obtained from the potential $U_A(x)$ and will be called S_A . Likewise the scattering matrix for a B-cell will be called S_B .

Another relation between the coefficients in the lattice can be obtained from the observation that the outgoing wave from a given cell is the incoming wave for the adjacent cell. This leads to the expressions

$$(III, 2) \quad \begin{aligned} b_+^n &= a_-^{n+1} \exp iad \\ b_-^n &= a_+^{n-1} \exp iad \end{aligned} ,$$

where $\alpha = \sqrt{2mE} / \hbar$ and d is the lattice spacing. These expressions take the place of the lattice sums that appear in the three-dimensional theory.⁶ It is of great importance in comparing the three-dimensional case with the one-dimensional case that the lattice sums for the former yield an expression for the incoming wave as the sum of the outgoing waves from all of the other cells, whereas equation (III, 2) is a sum over nearest neighbors only. Equations (III, 1) and (III, 2) yield the same information that is given by the transmission matrix R_n (cf. equation (I, 13)).

In a lattice that contains atoms of only one species (i.e., a pure crystal) all of the scattering matrices are the same. Also, Bloch's theorem (cf. equation (I, 1)) tells us that there exists a certain characteristic solution of the Schrodinger equation for a given energy which is of the form

$$(III, 3) \quad \psi_k(x) = u_k(x) \exp ikx ,$$

where $u_k(x)$ is a function with the periodicity of the crystal and k is the reduced wave number for the given energy. If we denote the solution in a given cell by $v_n(x)$, it can be shown from (III, 3) that

$$(III, 4) \quad v_n(x) = v_0(x) \exp -iknd .$$

The solution $v_n(x)$ is characterized by the coefficients in the n th cell. It is given by the linear combination of plane wave solutions with coefficients a_+^n and b_+^n in the region of zero potential on the right side of the cell (cf. equation (I, 4)), and by similar expression with the coefficients a_-^n and b_-^n in the region of zero potential to the left (cf. equation (I, 5)). Therefore, equation (III, 4) yields the following relations between the coefficients in the different cells:

$$\begin{aligned}
 a_+^n &= a_+^0 \exp -iknd \\
 b_+^n &= b_+^0 \exp -iknd \\
 (III, 5) \quad a_-^n &= a_-^0 \exp -iknd \\
 b_-^n &= b_-^0 \exp -iknd .
 \end{aligned}$$

From equations (III, 5) and (III, 2) a relation between the coefficients in the 0th cell can be derived and expressed in the following matrix form:

$$(III, 6) \quad \underline{b}^0 = M_0 \underline{a}^0 ,$$

where

$$(III, 7) \quad M_0 = \begin{pmatrix} 0 & \exp -i(k+\alpha)d \\ \exp i(k-\alpha)d & 0 \end{pmatrix} .$$

For this case (III, 1) yields

$$(III, 8) \quad \underline{a}^0 = S \underline{b}^0$$

where S is the scattering matrix for any cell of the pure crystal. A non-trivial solution of equations (III, 6) and (III, 8) exists if the equation

$$(III, 9) \quad \begin{vmatrix} S - M_0^{-1} \\ 0 \end{vmatrix} = 0$$

is satisfied. By solving equation (III, 9) an expression for the energy dependence of the reduced wave number, $k(E)$, can be found. This result was obtained in Chapter I by an investigation of the transmission matrix R_n .

For the random alloy Bloch's theorem is no longer valid. We assume, however, that the characteristic solution for a given energy extends throughout the lattice and look for a solution that has the form of a Bloch wave on the average. That is to say, we assume that for a given energy an effective reduced wave number, K , can be defined that will give the over-all phase of the solutions $v_n(x)$ (mentioned previously in connection with the case of the pure crystal) on the average. It is to be expected that in the random alloy there will be fluctuations in the phase of the solutions $v_n(x)$ about this average and that there will also be fluctuations in the norm of the solutions $v_n(x)$. We will try to take both of these things into account by introducing a set of (complex) quantities Θ_n such that if we write (in analogy with equation (III, 4))

$$(III, 10) \quad v_n(x) = \hat{v}_n(x) \exp -i(Knd - \Theta_n) ,$$

then the difference between the functions $\hat{v}_n(x)$ in two A-cells can be attributed to the local arrangement of the atoms while the quantities Θ_n take into account the long-range fluctuations throughout the lattice.

Since the coefficients a_+^n , b_+^n , etc. characterize the function $v_n(x)$, it follows from equation (III, 10) that the function $\hat{v}_n(x)$ is characterized by coefficients defined in the following way:

$$(III, 11) \quad \begin{aligned} a_+^n &= \hat{a}_+^n \exp -i(Knd - \Theta_n) \\ b_+^n &= \hat{b}_+^n \exp -i(Knd - \Theta_n) \\ a_-^n &= \hat{a}_-^n \exp -i(Knd - \Theta_n) \\ b_-^n &= \hat{b}_-^n \exp -i(Knd - \Theta_n) . \end{aligned}$$

The average of the coefficients $\hat{a}_+^n$ over all of the A-cells is given by

$$(III, 12) \quad \hat{a}_+^A = \frac{1}{NC_A} \sum_{n \in A} \hat{a}_+^n ,$$

where N is the (arbitrarily large) number of atoms in the crystal. In a like manner the average coefficients $\hat{b}_+^A$, $\hat{a}_+^B$, $\hat{b}_+^B$, etc. can be obtained.

A criterion for choosing the quantities K and Θ_n is that the average coefficients will remain finite. This criterion requires that the leading term of the phase in

each cell must be given by $(Knd - \theta_n)$ because otherwise the average coefficients would be zero. From the definition of the effective reduced wave number, K , it follows that the real parts of the θ_n must be symmetrically distributed about zero. It is assumed that the imaginary parts of the θ_n can be chosen such that the coefficients $\hat{a}_+^n$, $\hat{b}_+^n$, etc. are of the same order of magnitude in each cell.

The average of the functions $\hat{v}_n(x)$ over all of the A-cells is of course a solution of the Schroedinger equation with the potential of the A-cell, $U_A(x)$, since each of the functions individually has this property. Thus if a vector notation for the average coefficients is introduced in analogy with the one that we have been using (cf. equation (I, 6)) we can write

$$\begin{aligned} \hat{\underline{a}}^A &= S_A \hat{\underline{b}}^A \\ \hat{\underline{a}}^B &= S_B \hat{\underline{b}}^B, \end{aligned} \quad \text{(III, 13)}$$

where S_A is the scattering matrix for an A-cell and S_B is the scattering matrix for a B-cell.

Another relation between the average coefficients can be found using equations (III, 2). Inserting the definitions (III, 11) into equations (III, 2) yields

$$\begin{aligned} \hat{b}_+^n &= \hat{a}_-^{n+1} \exp -i[(K-\alpha)d - (\theta_{n+1} - \theta_n)] \\ \hat{b}_-^n &= \hat{a}_+^{n-1} \exp i[(K+\alpha)d - (\theta_{n-1} - \theta_n)]. \end{aligned} \quad \text{(III, 14)}$$

These equations will now be averaged over all of the A-cells with the crucial assumption that the quantity $(\theta_{n+1} - \theta_n)$ is a random variable that is now correlated with the random variables $\hat{a}_+^n$ or $\hat{a}_-^n$. We obtain from this operation

$$(III, 15) \quad \begin{aligned} \hat{b}_+^A &= Q(C_A \hat{a}_-^A + C_B \hat{a}_-^B) \exp -i(k-\alpha)d \\ \hat{b}_-^A &= Q(C_A \hat{a}_+^A + C_B \hat{a}_+^B) \exp i(k-\alpha)d , \end{aligned}$$

where

$$(III, 16) \quad Q = \frac{1}{NC_A} \sum_{n \in A} \exp i(\theta_{n+1} - \theta_n) .$$

We will now assume that the real part of the complex quantity $(\theta_{n+1} - \theta_n)$ is uncorrelated with the imaginary part. Using the fact that the real parts for different values of n are symmetrically distributed about zero, one sees that the average, Q , shown in equation (III, 16) is real. Summation over all cells containing B atoms yields

$$(III, 17) \quad \begin{aligned} \hat{b}_+^B &= \hat{b}_+^A \\ \hat{b}_-^B &= \hat{b}_-^A . \end{aligned}$$

From equations (III, 15) and (III, 17) it follows that

$$(III, 18) \quad \hat{\underline{b}}^A = Q M_0 (C_A \hat{\underline{a}}^A + C_B \hat{\underline{a}}^B) = \hat{\underline{b}}^B ,$$

where the vector notation was explained in connection with equation (III, 13). The matrix M_0 is given by equation (III, 6), and the real quantity Q is the average shown in equation (III, 16).

For the three-dimensional case equations (III, 14) are replaced by a sum over all of the lattice points in the crystal. This means that the interfering waves come from all directions, and it is to be expected that the coefficients of the incoming waves to the n th cell will be better behaved for this case. Also, since the interfering waves traverse a long distance through the lattice, the phase difference can be assumed to be due to many small causes and are thus better random variables.

We will now define a real quantity, q , by the relation

$$(III, 19) \quad Q = \exp qd \quad ,$$

and a matrix, M , by the relation

$$(III, 20) \quad M = M_0 \exp qd \quad .$$

Using these definitions, the requirement that equations (II, 13) and (II, 18) have non-trivial solutions may be written in the form:

$$(III, 21) \quad |c_A s_A + c_B s_B - M^{-1}| = 0 \quad .$$

Equation (III, 21) is the analogue of equation (III, 9) which is valid for the case that all of the atoms in the lattice are of one species (the pure crystal). The energy dependence of the quantity $q(E)$ as well as the energy dependence of the effective reduced wave number, $K(E)$, can be found from the complex equation (III, 21).

An explicit solution of equation (III, 21) can be obtained for the case of δ -function potentials with potential strengths V_A and V_B . The scattering matrices, S_A and S_B , are given for this case by equation (I, 20). The result is

$$(III, 22) \quad \coth qd = \frac{F^2 + (\alpha d)^2}{C_A C_B \Delta^2} \left[1 + \frac{F V_A V_B + \langle V \rangle (\alpha d)^2}{F^2 + (\alpha d)^2} \frac{\cot \alpha d}{\alpha d} \right]$$

and

$$(III, 23) \quad \begin{aligned} \cos Kd &= \cosh qd \left(\cos \alpha d - \frac{\langle V \rangle}{\alpha d} \sin \alpha d \right) \\ &+ \sinh qd \left(\frac{F}{\alpha d} \sin \alpha d + \frac{V_A V_B}{(\alpha d)^2} \cos \alpha d \right), \end{aligned}$$

where

$$(III, 24) \quad \begin{aligned} \langle V \rangle &= C_A V_A + C_B V_B \\ F &= C_B V_A + C_A V_B \\ \Delta &= V_A - V_B \end{aligned}$$

A calculation of the quantities $q(E)$ and $K(E)$ on the basis of equations (III, 22) and (III, 23) has been carried out for the choice $V_A = \pi$, $V_B = \pi/2$, and $C_A = C_B = 1/2$. The results of this calculation are shown in Figures 16 and 17. There are energy gaps on these figures for which no values for qd or $\cos Kd$ are given. In these gaps $q(E)$ is complex (being given by the logarithm of a negative number). The gaps occur in the forbidden zones of the random alloy and are thus of no interest in a discussion of the band structure.

In Figure 16, the quantity $\cos Kd$ is shown by the solid line and compared with $\cos kd$ given by the Nordheim-Muto theory for the same choice of potential strengths and concentrations (cf. equations (I, 23) and (I, 24)). A comparison of $\cos Kd$ with the quantity $\cos \theta$ that is given by the direct method of Chapter II (cf. Figure 14) shows that the two methods give similar results for the allowed zone in the energy range $1 < E < 4$. The results are quite different in the negative energy region, which is not surprising since the wave functions are localized about the atoms for this case (for a discussion of this effect, see reference 8) and the assumptions used in the intuitive method are no longer valid.

The matrix M defined in equation (III, 20) can be obtained from the equation for the matrix M_0 , (III, 6), by

Figure 16 : The Energy Dependence of $\cos Kd$.

Figure 17 : The Energy Dependence
of qd .

replacing the quantity α in (III, 6) with a complex quantity α' given by

$$(III, 25) \quad \alpha' = \alpha + iq \quad ,$$

where q is given in equation (III, 19). Using this fact it can be seen from a comparison of equations (III, 21) and (III, 9) that the energy dependence of the effective reduced wave number for a random alloy, $K(E)$, can be obtained from the consideration of a periodic lattice with the following properties: (1) The scattering matrix for each atom is the average scattering matrix $C_A S_A + C_B S_B$. (2) The electrons propagate in the regions of zero potential between the atoms with a complex wave number α' . The quantity α' corresponds to the complex energy discussed by Korringa.⁶

Chapter IV

DISCUSSION OF RESULTS

From the results of Chapters II and III, a density of allowed electronic states can be calculated and compared with "experiment." The only "experimental" results that are available for a one-dimensional random alloy appear in the paper by Landauer and Helland¹⁰ that was mentioned in Chapter I.

They considered an array of 150 square well potentials equally divided among two different well depths. The two kinds of wells were equally spaced along the x-axis in a more or less random sequence. By using a high-speed computer they found the number of allowed states below a given energy, $N(E)$, for a large number of energies. We will first compare the results of the direct method (Chapter II) with these numerical computations and then see how the results of the intuitive method (Chapter III) differ from this.

Some type of boundary conditions must be put on the problem if the density of states is to be calculated. If the reduced wave number k is known as a function of

energy, so that the solution in the N th cell may be obtained from (cf. equation (I, 18))

$$(IV, 1) \quad \underline{e}_N = \underline{e}_0 \exp iNkd \quad ,$$

the simplest boundary conditions to use are the periodic boundary conditions which require $\underline{e}_N = \underline{e}_0$. This gives the result that allowed states occur for values of kd which are integral multiples of $2\pi/N$. However, for every solution corresponding to a positive k , there is also one corresponding to a negative k . Thus, the total number of allowed states is given by the number of times that kd takes on a value given by an integral multiple of π/N . From this it follows that if the function $\cos kd$ takes on the value $(\cos kd)_1$ at an energy E_1 and the value $(\cos kd)_2$ at an energy E_2 and varies continuously and monotonically with the energy in the region $E_1 < E < E_2$, then the number of states with energies between E_1 and E_2 is given by

$$(IV, 2) \quad N_{12} = \frac{|(\cos kd)_2 - (\cos kd)_1|}{2} N \quad .$$

Using this equation one finds, for example, that the number of allowed states in an allowed zone of the pure A or pure B crystal is N , since the function $\cos kd$ varies monotonically from one to minus one for this case (cf. Figure 2).

Since the quantities Θ and Kd are the analogues for a random alloy of the quantity kd , we will use (IV, 2) to find the density of states for the random alloys. In Figure 18, the allowed bands and the number of states in each are shown for a pure A crystal, a pure B crystal, and the random AB crystal with the concentration $C_A = C_B = 1/2$ calculated by (1) the exact method of Chapter II, (2) the intuitive method of Chapter III, (3) the virtual crystal approximation of Nordheim and Muto. Since the calculations of Landauer and Helland were carried out for square well potentials whereas the ones presented here are for δ -functions, only the general features of the results may be compared.

The most striking result is the prediction by the direct method that in the region of negative energies where the B crystal has an allowed band while the A crystal does not, there will be an allowed band for the random AB crystal which contains a number of states equal to the number of B atoms (the factor of $1/2$ in Figure 18 is due to the fact that the calculations were carried out for equal concentrations of A and B atoms as is shown by equation (II, 74)). This result checks with the machine calculations and is explained by the observation that there should be localized states associated with the bound state of the B atom for which the wave function is

Figure 18: The Energy Bands.

large in the neighborhood of the B atoms (cf. reference 10). A similar effect appears in the negative energy region where the A crystal has an allowed band and the B crystal does not.

In the positive energy region, it is seen that the high-energy limit on the allowed band is between the ones for pure A and pure B crystals. An investigation of the form of $\cos \theta$ (Figure 14 in Chapter II) shows that the density of states is very low in the singly forbidden zone, where the A crystal has gone into a forbidden zone while the B crystal has not. The Nordheim-Muto theory also predicts that the random AB crystal will have an allowed band when one of the constituents does not; but the investigation of Figure 14 shows that this theory predicts that the density of states will go to zero sharply at the high-energy end, while the exact method gives a slower "tailing off." This effect is in general agreement with the machine calculations of Landauer and Helland and is also in agreement with estimates of the correction to the Nordheim-Muto theory due to higher-order terms in the perturbation expansion.

Another result of the direct method is to give a quantitative criterion for the appearance of forbidden zones in the random alloy which is more restrictive than the qualitative one proved by Luttinger.¹² The nice feature of the direct method is that this criterion, as

well as the other information shown on Figure 18, can be obtained by an investigation of the discriminant of the cubic equation (II, 38) alone. Of course for detailed information about the density of states within an allowed band it is necessary to find the saddle points and evaluate θ by means of equation (II, 53).

It is interesting to see from Figure 15 that for the allowed band in the positive energy region γ is extremely small until the singly allowed zone is reached and there it increases smoothly. In the negative energy region γ is much larger. These results indicate that the interpretation of γ as an average damping factor is justified.

From Figures 14 and 16 it is seen that the results from the intuitive method fall between those from the direct method and the Nordheim-Muto approximation. That there is any agreement at all seems rather encouraging, since the approximations developed for three dimensions will be less applicable to a one-dimensional model. The correction to the Nordheim-Muto theory for the high-energy end of the allowed bands is in the proper direction to give a slower tailing off. The quantity q_d that appears in the intuitive method probably has the same origin as the γ that appears in the exact method, and the two compare reasonably well for positive energies. One should

expect that since the method gives reasonable results in one dimension then it is a-fortiori so in three dimensions where the interfering waves come from all of the lattice points (rather than just from nearest neighbors) and where large clusters of like atoms are less likely to occur.

Thus, it appears that either of these methods is an improvement over existing methods for investigation of the band-structure in one dimension. The results of the direct method are undoubtedly far better than those of the intuitive method, but a generalization of this treatment to three dimensions would not be straightforward.

The direct method can, however, be generalized to treat other one-dimensional problems of interest. In deriving the expression for $\langle P \rangle$ shown in equation (II, 18), the only restriction imposed on the A and B matrices was that $\det A = \det B = 1$. There are many other cases that can be considered for which the A and B matrices have this property. For example, the length of the unit cells of the A and B atoms may be different or the potential of one of the atoms may be zero. The matrix $\langle P \rangle$ for a random alloy made up of more than two constituents can be found from a multiple contour

integral by a method analagous to that used in deriving (II, 18). These examples serve to show the flexibility of the direct method in treating one-dimensional problems. Other generalizations will undoubtedly occur to an investigator who wishes to use the method.

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AUTOBIOGRAPHY

I, John S. Faulkner, was born September 30, 1932, in Memphis, Tennessee; the son of William Oliver and Willella Aycock Faulkner. I received elementary school training in Memphis, Tennessee, where I was graduated from Central High School in 1950. In 1950 I enrolled in Maryville College, but transferred in 1952 to the Alabama Polytechnic Institute from which I was graduated with a B. S. degree in physics in June of 1954. I entered the graduate school of the Alabama Polytechnic Institute in September of 1954 and received a M. S. degree in physics in September of 1955. I entered the graduate school of The Ohio State University in September of 1955 to work toward a Ph.D. degree in physics. I married Mary Alice Crouch of Atlanta, Georgia, on June 12, 1957.